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HOT CARRIER PHENOMENA IN SEMICONDUCTORS AT MICROWAVE FREQUENCIES

THIRD QUARTERLY REPORT

NOVEMBER 15, 1961 --- FEBRUARY 15, 1962

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UNITED STATES ARMY

RESEARCH AND DEVELOPMENT LABORATORY

FORT MONMOUTH, NEW JERSEY

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PURPOSE

The objectives of this program are: (1) to learn more about physical phenomena, such as disturbances in carrier concentration and nonlinearities in complex conductivity, in homogeneous semiconductors at microwave frequencies under conditions in which the mean energy of the charge carriers is increased beyond thermal, and (2) to evaluate the possibilities for new microwave devices based on the effects found during the investigation.

ABSTRACT

By means of simple kinetic theory considerations an expression is derived for the diffusion constant $D^{(i)}$ of thermal carriers in the i^{th} valley of a many-valley semiconductor. $D^{(i)}$ is seen to be a tensor, the $\alpha\beta$ -component of which is $\langle \tau v_\alpha v_\beta \rangle$, where τ is the relaxation time and v_α the α^{th} component of the velocity. The Einstein relation is shown to hold between $D^{(i)}$ and $\mu^{(i)}$, the mobility tensor for the i^{th} valley. In n-Ge intervalley scattering is sufficiently rapid so that the actual diffusion rate depends on the average of $D^{(i)}$ over the valleys, which is a scalar. It is shown that the same result is obtained for the diffusion constant $D^{(i)}$ when a high electric field is applied perpendicular to the concentration gradient, except that the average must be taken over the actual energy distribution of carriers in the high field. The average diffusion constant D is calculated as a function of dc electric field intensity for n-Ge at 300°K . It is shown that at 3 kMc the time variation of the field is slow enough so that the instantaneous D for a field E should be equal to D for a dc field of the same magnitude.

For the measurements of recombination in high electric fields the method of injection has been changed from surface illumination by white light to injection at a contact in the massive end of the sample. This has several important advantages: (1) the carriers are distributed much more uniformly over the cross section of the sample; (2) it has been possible to eliminate sweepout; (3) samples with lower lifetimes can be measured than was previously the case.

The effect of high microwave fields on recombination has been looked for in samples with lifetime determined mainly by the rate of diffusion to the surface. Contrary to our expectations, no effect was

found up to 7500 volts/cm. It is thought that this is due to a decrease in surface recombination velocity compensating for the increase in diffusion rate.

Data on recombination in high microwave fields were obtained on additional copper- and nickel-doped p-Ge samples using the contact injection technique. These data are for the most part similar to those obtained earlier with the other technique. Since surface recombination cannot be eliminated entirely in these samples, its effects are being studied in order to correct for them.

The rf conductivity and dielectric constant at 69.25 kMc vs dc bias field have been measured for two additional samples, a 12 ohm-cm n-Ge sample and an 8 ohm-cm p-Ge sample. For the most part the data are similar to those obtained in the past on similar samples. In the case of the n-type sample there are some anomalies that may be due to injection from the conical part of the sample just above the thin filament. It should be possible to eliminate this by gold plating the conical region. Complete evaluation of the data on these samples is being deferred until more reliable corrections for the rf spreading resistance in the conical ends can be made.

Preparation of InSb samples by electrical discharge machining has been started.

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

A conference was held with Dr. Mette, the contract representative, at the General Telephone and Electronics Laboratories, Bayside, on November 24, 1961; E. Conwell, V. Fowler and J. Zucker were present. Progress under the present contract and future plans were discussed.

1. FACTUAL DATA AND CONCLUSIONS

1.1 DIFFUSION OF EXCESS CARRIERS IN A MANY-VALLEY BAND STRUCTURE

1.1.1 Introduction

For a gas of molecules the diffusion constant D is a scalar quantity that can be defined by the equation

$$\underline{j} = -D\Delta n, \quad (1.1)$$

where \underline{j} is the molecule current density that flows due to a concentration gradient Δn . Simple kinetic theory considerations lead to a relation between D and the properties of the molecules:¹

$$D = \frac{\langle \ell v \rangle}{3} = \frac{\langle \tau v^2 \rangle}{3} = \frac{2 \langle \tau \epsilon \rangle}{3m}, \quad (1.2)$$

where ℓ is the mean free path, v the speed, ϵ the energy, m the mass and $\tau = \ell/v$. The averages indicated are to be taken over the velocity distribution of the molecules. Equations (1.1) and (1.2) hold also for the diffusion of conduction electrons or holes inside a semiconductor with the simple model of the band structure, provided, of course, injection is small enough so that the carriers diffuse independently.² The quantity m in (1.2) must in this case be replaced by m^* , the effective mass. For a semiconductor with a many-valley band structure,³ however, the equations must be modified, and this will be carried out in section (1.1.2) for the case of thermal carriers. In section (1.1.3) some effects of applying high electric fields will be considered. It will be assumed throughout that τ is a function of ϵ only, i.e., any anisotropy of τ will be neglected. This has been shown by Herring to be a good

approximation for electrons in Ge scattered by lattice vibrations,³ and would therefore be valid for the samples and temperatures we have been using in the recombination studies.

1.1.2 Diffusion of Thermal Carriers

For a simple many-valley model the energy of an electron with wave vector \underline{P} measured from the valley minimum can be written

$$\epsilon(\underline{P}) = \frac{P_1^2}{2m_1^*} + \frac{P_2^2}{2m_2^*} + \frac{P_3^2}{2m_3^*} \quad (1.3)$$

where m_1^* , m_2^* and m_3^* are the effective masses and P_1 , P_2 and P_3 the components of \underline{P} in the three coordinate directions that are principal axes for the constant-energy surfaces of the valley. When the electron density is small enough for Maxwell-Boltzmann statistics to be valid, the thermal equilibrium distribution function for electrons in the i^{th} valley can be written

$$f_o^{(i)} = e^{\frac{-\epsilon_F}{kT}} e^{\frac{-\epsilon(\underline{P}^{(i)})}{kT}} \quad (1.4)$$

where ϵ_F , the Fermi energy, is to be measured from the conduction band edge. This can be rewritten in terms of the carrier density $n^{(i)}$ in the i^{th} valley using the fact that

$$n^{(i)} = \sum_{\underline{P}^{(i)}, s} f_o^{(i)}, \quad (1.5)$$

the summation being taken over all $\underline{P}^{(i)}$ in the i^{th} valley in a unit volume of material and over both signs of spin. With (1.5) we can write (1.4) as

$$f_0^{(i)} = n^{(i)} \frac{e^{-\epsilon(\underline{P}^{(i)})/kT}}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} \quad (1.6)$$

We wish now to consider the case of material in a steady state at the temperature T with a concentration gradient $\Delta n^{(i)}$ that we take to be in the $+x$ direction. It will be assumed that the variation in $n^{(i)}$ is small over a mean free path. The distribution function can then be written

$$f_0^{(i)}(x) = n^{(i)}(x) \frac{e^{-\epsilon(\underline{P}^{(i)})/kT}}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} \quad (1.7)$$

Because of the concentration gradient, at any plane $x = x_0$ there will be a net current of electrons flowing in the direction of $-x$. To calculate this current it will be assumed, as is customary,¹ that the properties of an electron found at x_0 are characteristic of the x at which its last collision occurred. If \hat{x} denotes a unit vector in the $+x$ direction, on the average the electrons found at x_0 will have had their last collision at $x_0 - \hat{x} \cdot \underline{v} \tau$ for either direction of motion. The particle current density of electrons in the i^{th} valley crossing x_0 in the $+x$ direction is then

$$j_+^{(i)}(x_0) = \sum_{\underline{P}^{(i)}, s}^+ f_0^{(i)}(x_0 - \hat{x} \cdot \underline{v} \tau) \underline{v}, \quad (1.8)$$

where the + on the summation sign indicates that the summation is to be taken only over electrons with a component of \underline{v} in the +x direction.

Similarly, the current density crossing x_0 in the -x direction is

$$j_{-}^{(i)}(x_0) = \sum_{\underline{P}^{(i)}, s}^{-} f_0^{(i)}(x_0 - \hat{\underline{x}} \cdot \underline{v} \tau) \underline{v} . \quad (1.9)$$

Since we have assumed that the variation of f is small in the distance ℓ , we can take

$$\begin{aligned} f_0^{(i)}(x_0 - \hat{\underline{x}} \cdot \underline{v} \tau) &= f_0^{(i)}(x_0) - \hat{\underline{x}} \cdot \underline{v} \tau \left(\frac{\partial f_0^{(i)}}{\partial x} \right)_{x_0} \\ &= \frac{e^{-\epsilon(\underline{P}^{(i)})/kT}}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} \left[n^{(i)}(x_0) - \hat{\underline{x}} \cdot \underline{v} \tau \left(\frac{\partial n^{(i)}}{\partial x} \right)_{x_0} \right] \end{aligned} \quad (1.10)$$

When (1.10) is used for $f_0^{(i)}$ in (1.8) and (1.9), and the resulting expressions are added to give the net current $j^{(i)}(x_0)$, the terms in $n^{(i)}(x_0)$ cancel and we get:

$$j^{(i)}(x_0) = \frac{\sum_{\underline{P}^{(i)}, s} \left[e^{-\epsilon(\underline{P}^{(i)})/kT} \tau \underline{v} \cdot \Delta n^{(i)} \right]}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} . \quad (1.11)$$

By analogy with (1.1) we can define the coefficient of $\Delta n^{(i)}$ as the diffusion constant $D^{(i)}$ for carriers in the i^{th} valley. It is seen that $D^{(i)}$ is a tensor rather than a scalar. The components of $D^{(i)}$ are given by

$$D_{\alpha\beta}^{(i)} = \frac{\sum_{\underline{P}^{(i)}, s} \left[e^{-\epsilon(\underline{P}^{(i)})/kT} \tau v_{\alpha} v_{\beta} \right]}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} = \langle \tau v_{\alpha} v_{\beta} \rangle, \quad (1.12)$$

which is the analog of (1.2) for this case. Since by assumption τ is independent of position on the constant-energy surface, (1.12) can be simplified by replacing $v_{\alpha} v_{\beta}$ by its average over such a surface.

The components of the mobility tensor for the i^{th} valley are given by³

$$\mu_{\alpha\beta}^{(i)} = \frac{q}{kT} \frac{\sum_{\underline{P}^{(i)}, s} \left[e^{-\epsilon(\underline{P}^{(i)})/kT} \tau v_{\alpha} v_{\beta} \right]}{\sum_{\underline{P}^{(i)}, s} e^{-\epsilon(\underline{P}^{(i)})/kT}} \quad (1.13)$$

Thus

$$D_{\alpha\beta}^{(i)} = \mu_{\alpha\beta}^{(i)} kT/q. \quad (1.14)$$

This is the Einstein relation for the many-valley model.

It is useful to relate $D^{(i)}$ to the S tensor introduced earlier in the theoretical treatment of magnetoresistance and mobility in a many-valley semiconductor.⁴ For the case of spheroidal constant energy surfaces it is seen that

$$D_{\alpha\beta}^{(i)} = \left\langle \tau \bar{S}_{\alpha\beta}^{(i)} \right\rangle, \quad (1.15)$$

where $\bar{S}_{\alpha\beta}^{(i)}$ is given by eq. (24) of reference (4) with ω set equal to zero. With this it is possible to find $D_{\alpha\beta}^{(i)}$ quickly for any set of axes.

Using (1.15) and the results of reference (4), we find that in the principal axis system $D_{xx}^{(i)} = D_{yy}^{(i)} = 2 \langle \tau \epsilon \rangle / 3m_t$, while $D_{zz}^{(i)} = 2 \langle \tau \epsilon \rangle / 3m_l$, where m_t and m_l are effective masses for the longitudinal and transverse directions of the ellipsoids. These results can also be obtained from (1.12), using the fact that the average of $v_\alpha v_\beta$ over a constant energy ellipsoid is $(2\epsilon/3m_\alpha) \delta_{\alpha\beta}$. When m_l and m_t have quite different values, as is the case in germanium and silicon, the anisotropy of $D^{(i)}$ is quite considerable. To observe this anisotropy one might, at least in principle, perform an experiment in which electrons are injected at a point, and their diffusion rate measured by observing the current arriving at a second point within a diffusion length. If the valleys were oriented along the cube axes, for example, with m_l greater than m_t , and the second point displaced along the 100 direction from the first, we would expect to find that electrons from the 010 and 001 valleys would arrive first, together, and those from the 100 valley would arrive later. Such effects have never been observed in germanium or silicon because of the existence of intervalley scattering. In germanium the intervalley scattering rate has been found to be so high down to the lowest temperatures investigated, about 20° K, as to make it unlikely that any effects of the kind described could be seen at all. The intervalley scattering rate might, of course, be smaller in other materials. Even if it were not, however, it should be possible to observe effects of the anisotropy of $D^{(i)}$ if the equivalence of the valleys is destroyed by a shear or a high

electric field, for example. Such measures have, of course, made it possible to observe the anisotropy of the mobility tensor.^{3, 6}

When intervalley scattering is sufficiently rapid, the diffusion constant for any carrier is the average of $D^{(i)}$ over the valleys. Denoting this average by D , we have

$$D = \frac{1}{N} \sum_{i=1}^N D^{(i)} = \left\langle \tau \frac{1}{N} \sum_{i=1}^N \bar{S}^{(i)} \right\rangle, \quad (1.16)$$

where N is the number of equivalent valleys. The average of $\bar{S}^{(i)}$ over the valleys has been evaluated for a cubic crystal.⁴ In the absence of magnetic field it is a diagonal tensor with identical elements, so that the average diffusion constant becomes a scalar:

$$D = \frac{2 \langle \tau \epsilon \rangle}{3 m^{(I)}} \quad (1.17)$$

where $m^{(I)}$ is the interstitial mass,³ the reciprocal of the average of the reciprocals of the principal masses. It is seen that the Einstein relation holds between D and the average mobility μ . This has been verified experimentally in the Haynes-Shockley experiment.⁷

1.1.3 Predicted Effects in High Fields

We shall now apply some of the foregoing considerations to a situation similar to one we have used experimentally. Consider the case of a long thin filament with a high electric field, assumed time-independent for the moment, along its length, which is to be taken as the z -direction. The z -direction will be chosen to be a symmetry direction of the filament, in particular one with respect to which all valleys are symmetrically located, such as the 100 direction in Ge. It will be assumed also that the

bulk recombination rate of the filament is much smaller than its surface recombination rate, so that excess carriers must diffuse to the surface to recombine.

Let us denote the distribution function for the i^{th} valley in the field E by

$$f^{(i)}(E, \underline{x}) = n^{(i)}(\underline{x}) F(E, \underline{P}^{(i)}) / \sum_{\underline{P}^{(i)}, s} F(E, \underline{P}^{(i)}).$$

The current density in the $+x$ direction is then, according to the considerations of the last section,

$$j_+^{(i)}(\underline{x}_0) = \sum_{\underline{P}^{(i)}, s}^+ f^{(i)}(E, \underline{x}_0 - \hat{\underline{x}} \cdot \underline{v} \tau) \underline{v} \quad (1.18)$$

The current density in the $-x$ direction, similarly, is

$$j_-^{(i)}(\underline{x}_0) = \sum_{\underline{P}^{(i)}, s}^- f^{(i)}(E, \underline{x}_0 - \hat{\underline{x}} \cdot \underline{v} \tau) \underline{v} \quad (1.19)$$

Expanding $f^{(i)}$ as before, we have

$$f(E, \underline{x}_0 - \hat{\underline{x}} \cdot \underline{v} \tau) = f(E, \underline{x}_0) - \hat{\underline{x}} \cdot \underline{v} \tau \left(\frac{\partial f}{\partial \underline{x}} \right)_{\underline{x}_0}.$$

When the two currents are added, the terms in $f(E, \underline{x}_0)$ cancel because there is no asymmetry in the x direction. The net current density can then be written

$$j^{(i)}(\underline{x}_0) = - \sum_{\underline{P}^{(i)}, s} \frac{F^{(i)}(E, \underline{P}^{(i)})}{\sum_{\underline{P}^{(i)}, s} F^{(i)}(E, \underline{P}^{(i)})} \tau \underline{v} \underline{v} \cdot \nabla n^{(i)} = - \langle \tau \underline{v} \underline{v} \rangle_E^{(i)} \cdot \nabla n^{(i)} \quad (1.20)$$

where the subscript E indicates that the average is to be taken over the velocity distribution in the field E. Equation (1.20) gives the dependence of $D^{(i)}$ on E.

The form of the function F depends on the magnitude of the electric field intensity. For fields high enough so that an electron loses only a small part of its energy in a collision, $F^{(i)}$ can be written in the form $F_0^{(i)} + F_1^{(i)}$ where $F_0^{(i)}$ does not vary over a constant energy surface, i.e. $F_0^{(i)} = F_0^{(i)}(\epsilon)$, and $F_1^{(i)} \ll F_0^{(i)}$.⁴ It has been shown by Reik, Risken and Finger⁸ that $F_0^{(i)}(\epsilon)$ for n-Ge is a Maxwell-Boltzmann distribution over most of the energy range of interest for hot electrons, with only slight deviations for ϵ less than twice the optical phonon energy. Such small energies would correspond to fields less than about 2 kv/cm in Ge. Thus for fields greater than about 2 kv/cm we should be able to approximate $F(E, \underline{p}^{(i)})$ quite well by $e^{-\epsilon kT_e}$, where T_e is the electron temperature. $D^{(i)}$'s for the different valleys can be combined as before, since the field has been applied so as to produce the same temperature in every valley, and we obtain for the average diffusion constant in the field E

$$D(E) = \frac{2}{3m^{(I)}} \langle \tau \epsilon \rangle_E = \frac{\mu(E) kT_e}{q} \quad (1.21)$$

For fields less than 2000 volts/cm it is unfortunately not possible to write down any simple expression for F . Furthermore, it is no longer true that F can be well approximated by a function of energy only. When an electron loses most of its energy in a collision, the increase in velocity due to the field will be mainly in the field direction. This means, in the case we are considering, that the increase will be for the most part perpendicular to the diffusion current. Clearly, then, the effect of the high field on D will be smaller than if the increase were distributed more isotropically, as it is in higher fields. It should also be noted that, if the distribution is not a Maxwell-Boltzmann one, the Einstein relation is not satisfied.

To calculate D as a function of electric field intensity for n -germanium it is convenient to use the Einstein relation. Over the small range of fields for which it is not valid the changes in D are quite small in any case. If the subscript o denotes the value of a quantity in the absence of electric field, the Einstein relation gives:

$$\frac{D(E)}{D_o} = \frac{\mu(E)}{\mu_o} \frac{T_e}{T_o} \quad (1.22)$$

Using the theoretically calculated T_e/T_o for a given μ/μ_o , we can obtain $D(E)/D_o$. The field to which this value of the ratio corresponds is the

field at which $\mu(E)/\mu_0$ is observed. The values of $D(E)/D_0$ obtained in this way are shown as circled points in Fig. 1. It is seen that $D(E)$ is approximately a linear function of E over a wide range of fields. This results from the facts that the drift velocity is approximately constant in this range of fields, so that μ is essentially proportional to E^{-1} , while T_0 has been shown⁸ to be approximately proportional to E^2 .

In our experiments the field heating the carriers is an alternating field, of course, rather than a steady one. If the rate of variation of the field were slow enough, it is clear that $D(E)$ derived above would represent the instantaneous value of D . Specifically, in order for eq. (1.18) to be valid for the instantaneous field, the rate of variation of the field must be slow enough so that: (1) $f^{(i)}$ in the instantaneous E is the same as in the dc field E , and (2) $f^{(i)}$ has changed very little in the time τ . If τ is small enough compare to the period T of the microwave field, then both of these conditions should be satisfied. In the samples of interest the highest value of τ is $\sim 2 \times 10^{-13}$ second, so $\tau/T \leq 10^{-3}$, which should be small enough. Evidence that condition (1) is satisfied was obtained, of course, in our studies of the variation of mobility with field at 3 kMc. Thus the dashed line in Fig. 1 should represent well the variation of instantaneous D with field at 3 kMc.

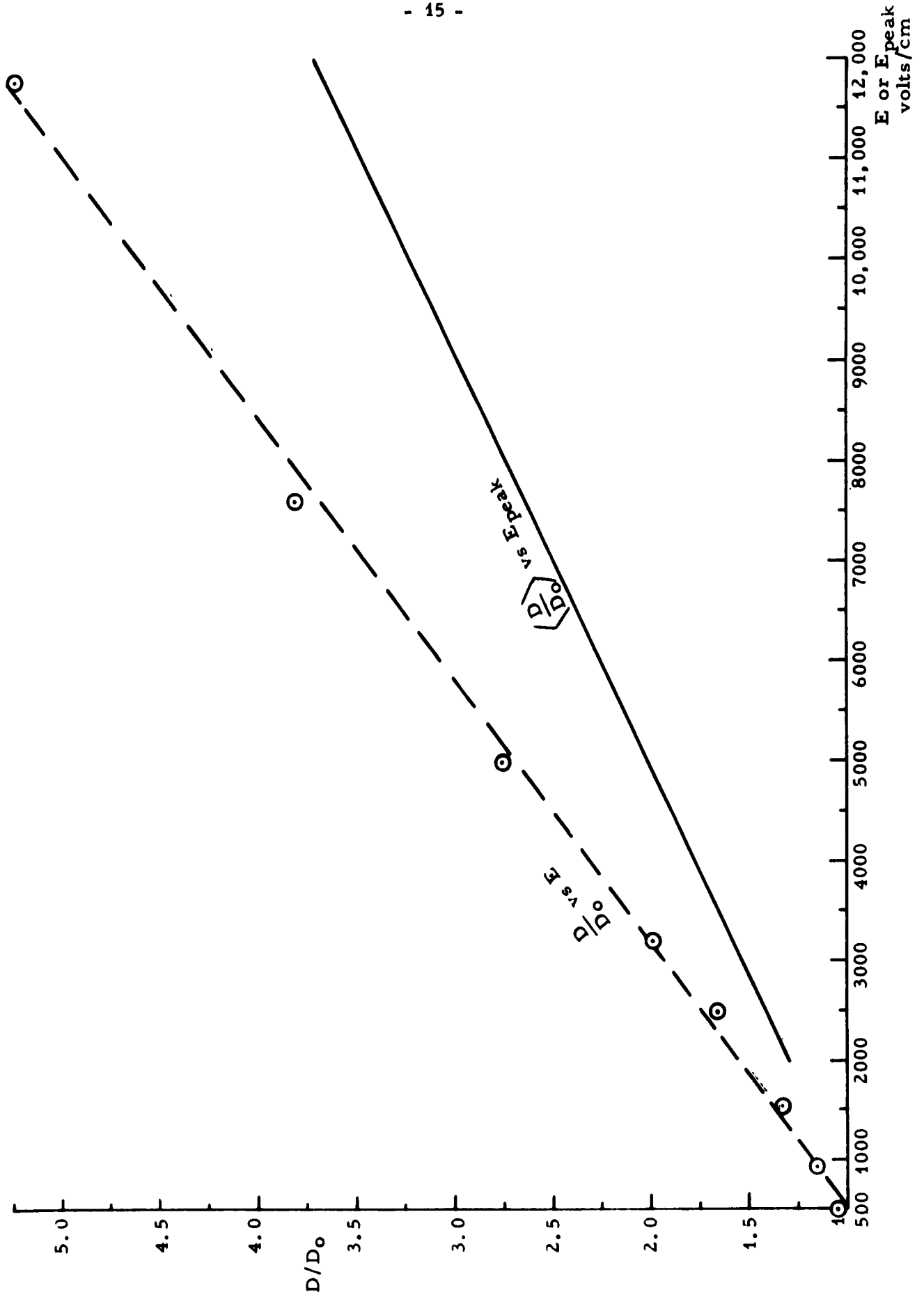


Fig. 1. Theoretical plots of D/D_0 vs E and average of D/D_0 over an rf cycle vs E_{peak} for n-Ge at 300°K.

Actually, it is expected that the quantity that can be obtained experimentally is the average of D over a microwave cycle. This average was calculated by fitting the dashed line of Fig. 1 to the appropriate linear function, and assuming $D/D_0 = 1$ below 550 volts/cm, where the dashed line cuts the E axis. The resulting average is the solid line in Fig. 1. It is seen that the expected changes in D are quite considerable.

1.2 INVESTIGATION OF RECOMBINATION OF HOT CARRIERS

1.2.1 Measurement Techniques and Samples

In order to produce a more uniform distribution of excess carriers in the samples, the mode of injection has been changed from surface illumination by white light, which, of course, is non-penetrating, to contact injection. To make this change possible, the sample design has been changed to that shown in Fig. 2. The massive end of the sample has been reduced to a disc about 10 mils thick, its diameter remaining 203 mils. An injecting contact is made at the center of this disc by etching a shallow depression at the center, placing a pellet of 95% Sn-5% Sb alloy (for p-type samples) into the depression and then heating the sample to 550°C in a forming gas atmosphere for two minutes. The ohmic contacts at both ends are made in the usual way by plating the end of the filament and most of the unetched portion of the disc with gold-gallium (for p-type samples) first, then nickel, and then heating as described above for alloying. The ohmic and injecting contacts are, of course, alloyed simultaneously. A small etched region, with low surface conductance, separates the injecting and ohmic contacts on the disc.

The starting material for the samples measured in this quarter is identical to that used in the last quarter. The samples are described in Table I. All samples are oriented in the 100 direction in order that

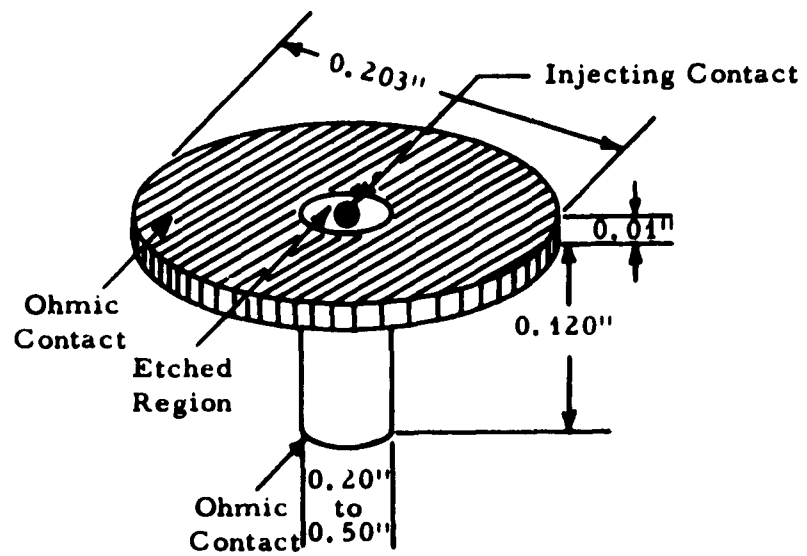


Fig. 2. Sample designed for measurements using the contact injection method.

TABLE I
CHARACTERISTICS OF SAMPLES

Sample	Concentration of majority impurity per cm ³	Recombination due to	Fermi level* eV	Low-field filament lifetime μ sec	Low-field bulk lifetime μ sec	Filament diameter mils
Cu-10a	1.92×10^{15}	$3 \times 10^{14} / \text{cm}^3 \text{ Cu}$	0.2	6.0	~ 15	42.8
Cu-10b	"	"	"	5.6	"	33
Cu-10c	"	"	"	4.6	"	29
Cu-11	"	"	"	5.5	"	47.6
Ni-3a	1.16×10^{15}	$1 \times 10^{14} / \text{cm}^3 \text{ Ni}$	0.22	13.1	-	39.5
Ni-3b	"	"	"	6.6	-	32.5
Ni-4	"	"	"	14.2	-	46.2
D-1	6.7×10^{14}	surface (high s produced by argon bombard- ment)	-	7.2	450	40
S-1	2.4×10^{15}	surface (pre- pared by CP-4 etch)	-	1.93	~500	11.6

* Measured from top of valence band

all valleys be heated equally. They are all p-type, the majority impurity being gallium. The filament diameters have been made larger than those of earlier samples in order to decrease surface effects.

In the new system, minority carriers are injected with a pulse applied to the injecting contact in the broad end of the sample. The microwave field is applied during the decay of the injected carriers, and the decay time constant during the microwave pulse is obtained by measuring the amplitude of the decay curve immediately before and after the microwave pulse. It would also be possible to measure the decay during the microwave pulse, but it is felt that the method adopted leads to greater precision because of unavoidable microwave pulse shape distortion and jitter, especially at the higher fields. It is of course assumed that the decay during the microwave pulse is exponential. This has been verified for fields low enough to permit accurate measurements on the pulse tops.

A diagram of the measurement apparatus is shown in Fig. 3. Two pulse generators are used, one to inject the carriers, the other to trigger the magnetron. The magnetron trigger is synchronized with the injection pulse generator. The pulse generators used (Teletronics type 200AA) allow for the delay or advance of the pulse with respect to the trigger. It is therefore possible to apply the microwave pulse at any desired time during the decay. The measured current is produced by a dc battery in series with an external resistance R_o . This is usually set equal to the sample resistance for maximum output. This dc current flows through the ohmic contacts. The battery polarity is the same as that of the injecting pulse, and causes those injected carriers that are in the disc part of the sample at the termination of the pulse to flow into the filament.

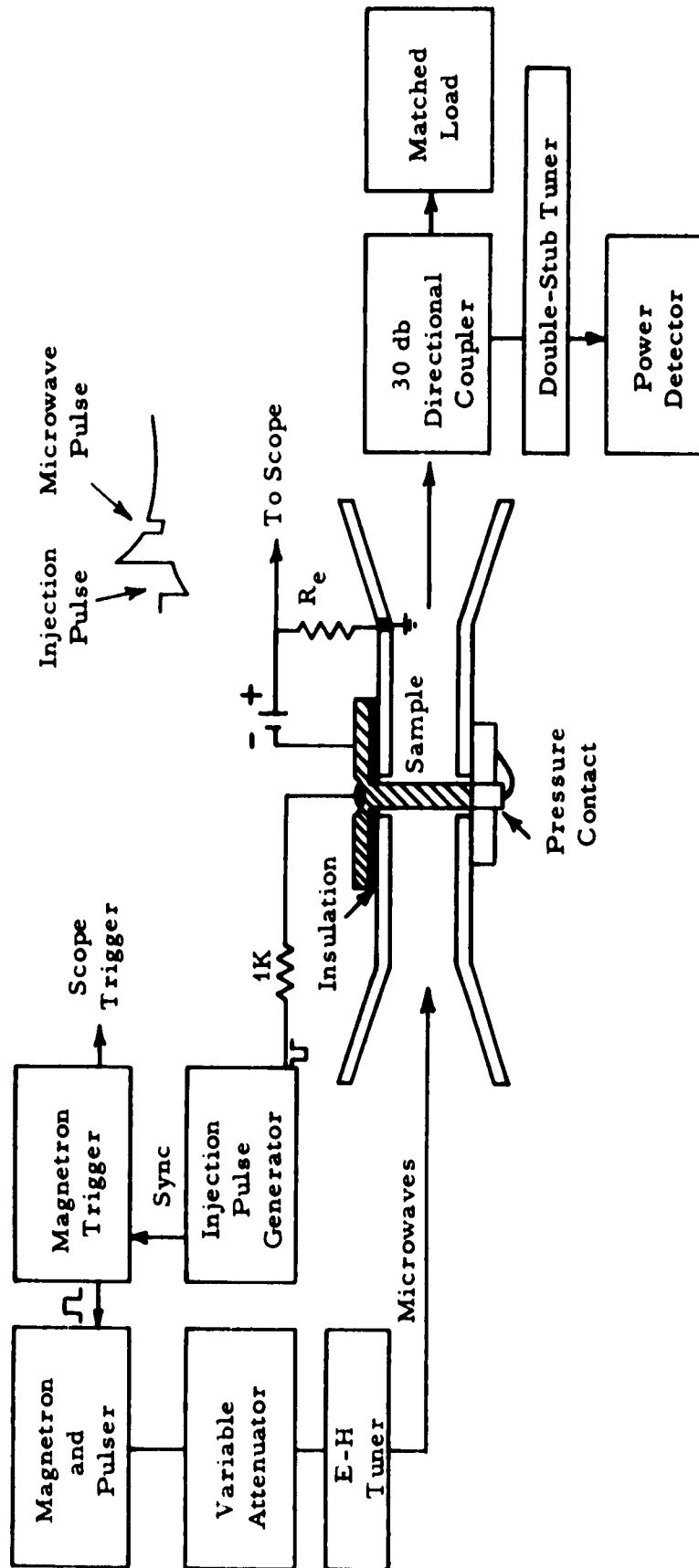


Fig. 3. Diagram of the measurement apparatus used in the contact injection method.

The data are obtained from photographs such as Fig. 4. Two traces are photographed for each value of the microwave field. The upper trace is the voltage across the resistor in series with the sample as a function of time with both the microwave field and the injection pulse on. The lower trace is the same voltage with the microwaves applied but with no injection. This latter trace constitutes the base line from which the amplitude of the decay curve is measured. This has the advantage that extraneous effects, such as change in resistance due to lattice heating or injection by the microwave pulse, can be



Fig. 4. Photograph of the oscilloscope display from which the measurements of decay time constants are made. The time scale is 5 microseconds per major division and the vertical sensitivity is 20 millivolts per major division.

eliminated since these effects should not be significantly altered by the addition of a relatively small number of injected carriers. τ_{mw} , the apparent decay time constant during the microwave pulse, is calculated from V_0 and V_1 , the vertical distances between the traces before and after the microwave pulse, respectively, with the formula

$$\tau_{mw} = t / \ln(V_0/V_1) \quad (1.2.1)$$

where t is the time in which the decay amplitude falls from V_0 to V_1 .

A major advantage of the new technique is that it has made possible the complete elimination of sweepout. When, as previously, injection is by illumination along the filament, the carriers created near the end of the filament are being continuously swept out by the dc field. This introduces errors since the mobility, and hence the rate of sweepout, are different during the microwave pulse from what they are in the absence of the pulse. In the present technique all minority carriers are introduced at one end; it is therefore possible by correct choice of the injection pulse width and amplitude and dc sweep field to insure that no injected carriers reach the other end during the microwave pulse. The relation between the parameters required to achieve this condition can be stated mathematically by expressing T_{max} , the maximum injection pulse width for which no sweepout will occur during the microwave pulse, in terms of: E_{dc} , the dc field across the sample; E_p , the injection pulse field; L , the length of the sample; t_a , the time between the end of the injection pulse and the end of the microwave pulse; and μ_0 , the zero-field mobility of the injected carriers. This relation is

$$T_{max} = \frac{L}{\mu_0(E_{dc} + E_p)} - \frac{t_a E_{dc}}{(E_{dc} + E_p)} = \frac{L - d}{\mu_0(E_{dc} + E_p)} \quad (1.2.2)$$

where $d = t_a \mu_o E_{dc}$. The first term on the right of 1.2.2 represents the time necessary to sweep injected carriers the entire length of the filament in the combined dc and pulse fields. The quantity d represents the distance the injected carriers move in time t_a in the dc field alone. $L-d$ is therefore the maximum allowable distance the combined dc and pulse fields may sweep the injected carriers such that no sweepout occurs until after the microwave pulse is over. The time $L/\mu_o(E_{dc} + E_p)$ is measured directly on the oscilloscope by increasing the injection pulse width until the injected current saturates. When this occurs, the injected carriers have reached the end of the filament, and the distribution of excess carriers along the filament reaches a steady state. For the recombination measurements the injection pulse width is typically set at between $1/2$ and $2/3$ the maximum pulse width calculated from equation 1.2.1.

It is well known that only for small injection are the equations that describe the recombination processes in a semiconductor linear.² An exponential decay, independent of the distribution of excess minority carriers in the sample, is obtained, therefore, only for small injection. Experimentally we have found that the dependence of decay time constant on injection level vanishes for excess current less than about 10% of the ohmic current. All measurements are therefore made after the injected current has decayed to this amount. To determine when this point has been reached, the following relation between γ , the ratio of injected to ohmic current, and ΔV , the amplitude of the decay curve is used

$$\Delta V = \frac{\gamma V_e}{1 - \gamma + V_e/V_s} \quad (1.2.3)$$

where V_s is the voltage across the sample and V_e is the voltage across the resistance in series with the sample.

Because of the finite bandwidth of the oscilloscope and the finite rise and fall times of the microwave pulse, the decay of injected current from which τ_{mw} is to be obtained is measured over an interval in part of which the lifetime is actually equal to its zero-field value. A correction must therefore be applied to extract the actual value of τ_{mw} from the measured decay. The situation is depicted in Fig. 5. It is easily seen that the actual value of the ratio of zero-field lifetime to lifetime in the microwave field, τ_o / τ_{mw} , is given by

$$\frac{\tau_o}{\tau_{mw}} = \frac{t}{T} \left[\left(\frac{\tau_o}{\tau_{mw}} \right)_{app} - 1 \right] + 1 \quad (1.2.4)$$

where t is the interval over which the decay is measured, T is the microwave pulse width and $(\tau_o / \tau_{mw})_{app}$ is the ratio calculated assuming $t = T$.

It has been found that, in addition to the advantages of more uniform minority carrier distribution over the cross section and the elimination of sweepout, the new technique has made it possible to measure samples with much lower lifetimes than could be done before. For example, it is now possible to measure samples with diffusion-limited lifetime. This was not previously possible because of the small photoconductivities of such samples when surface illumination was used for carrier injection. The lower limit on the lifetime that can be measured by using this technique is set by the fall time of the injection pulse, which is 0.1 microsecond with the present equipment.

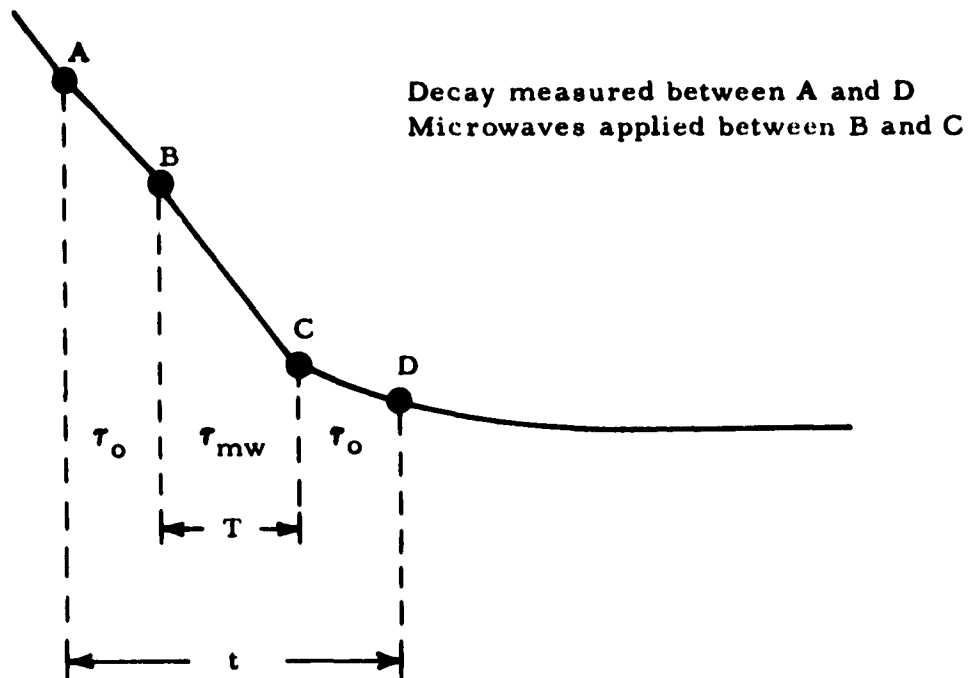


Fig. 5. Details of the decay during the measured time interval.

1.2.2 Results

1.2.2.1 Diffusion-limited Lifetime

A major impetus to the development of the new measurement techniques was the desire to measure the effect of high fields on lifetime determined by the rate of diffusion of injected carriers to the surface of the sample. This requires high surface recombination velocity, which is best achieved by using samples with rough surfaces. Unfortunately, rough surfaces invariably break down in microwave fields greater than about 1 kv/cm. Therefore, samples with rough surfaces could not be used for these studies. Instead, a sample (D-1) with an etched surface that had been bombarded with argon ions was used. Sample D-1 was first etched in CP-4 and then bombarded at an argon pressure of 0.2 mm Hg for 2000 μ a-secs. The resulting surface recombination velocity as calculated from the measured lifetime, 7.2 μ -sec, and filament diameter, 40 mils, was 8300 cm/sec. This value of surface recombination velocity is, unfortunately, not high enough to give a filament lifetime dependent only on diffusion constant. To our surprise, no change in filament lifetime of this sample was found, within experimental accuracy, up to microwave fields of 7500 volts/cm. As indicated earlier, sizeable increases in the diffusion constant were expected, and in previous work samples with surface-limited lifetime, measured in the old way with injection by illumination with white light, always showed decreases in lifetime in the high microwave fields. The only difference between sample D-1 and surface-limited samples previously reported, aside from surface treatment, is in orientation: sample D-1 is oriented in the 100 direction while the previous samples were oriented in the 110 direction. In order to compare surface behavior of sample D-1 and the 110-oriented samples, D-1 was etched to restore a relatively low-surface. This enhances the

effect of variations in s and decreases the contribution of D variations. The change in steady-state photocurrent as a function of microwave field intensity was then measured using non-penetrating white light for injection, which further enhances the importance of s . It was found, in contrast to the 110-oriented samples, that the photocurrent increased on application of the microwave field, implying a decrease in s with field. A possible interpretation of the absence of change in τ_{mw} found for sample D-1 is, therefore, that the decrease in s compensates for the increase in D .

1.2.2.2 Bulk Lifetime

The data taken on samples with bulk-limited lifetime are plotted in Fig. 6. The results are consistent with those obtained on similar samples in the last quarter using injection by surface illumination. As before, the recombination is increased for samples with copper recombination centers, while it is decreased for those with nickel recombination centers. The greatest differences between the data taken with the new technique as compared with the old are to be found in the copper-doped samples Cu-10 and Cu-11. The present data show a monotonic decrease of lifetime with increasing field intensity, while one of the samples measured in the last quarter, Cu-4, had a photocurrent that first decreased and then increased as the field was increased. The difference between the two sets of data appears to arise from different contributions of the surface recombination to the total filament lifetime for the two cases, which may be due to the different measurement techniques as well as to different filament dimensions. In order to get a better idea of the effect of surface recombination, data have been taken on the same sample with different filament diameters. These data are shown in Fig. 6. The diameter was reduced after each run by etching in CP-4, and it is seen that a change in diameter did change the results somewhat.

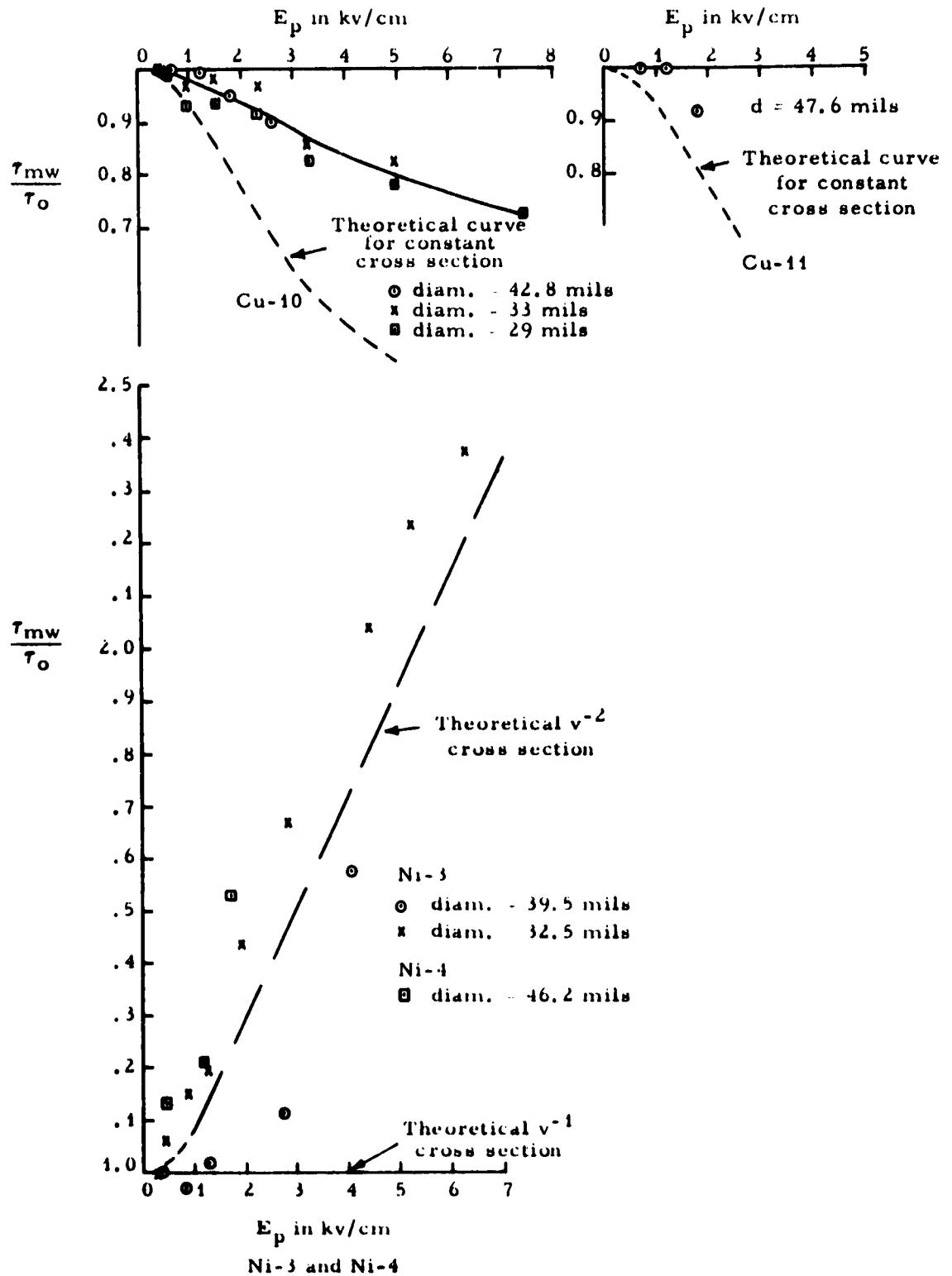


Fig. 6. Ratio of the decay time constant of contact-injected carriers in microwave fields relative to the zero-field decay time constant as a function of peak microwave field intensity for Cu- and Ni-doped p-type Ge.

In an attempt to isolate the surface contribution, a sample was prepared (sample S-1) having approximately the same carrier concentration and surface preparation as the copper- and nickel-doped samples but containing no intentionally introduced bulk recombination centers. Since the relatively small amount of copper or nickel in the bulk should not affect the surface, it is reasonable to expect that S-1 has surface properties similar to those of the copper- and nickel-doped samples. This has been borne out by comparison of S-1 and Cu-10. If the two samples had the same recombination centers, present in the same concentration, etc., the ratio of their surface recombination velocities should equal the ratio of their carrier concentrations. The surface recombination velocities are found to be 4×10^3 and 3×10^3 cm/sec for S-1 and Cu-10, respectively, while the carrier concentrations are 2.4×10^{15} and 1.9×10^{15} /cm³. The ratios agree within experimental error.

Measurements were made on S-1 of the effect on the lifetime of microwave fields up to about 10 kv/cm. No significant changes in lifetime were detected in this range of fields, making it appear that the surface lifetime of this type of sample is field-independent. This conclusion will be checked by measurements on additional samples. If it is correct, the correction for surface effects in the copper- and nickel-doped samples can be made very simply.

1.3 COMPLEX CONDUCTIVITY INVESTIGATION

1.3.1 Measurements on n-Ge and p-Ge Samples

Work was continued during this quarter on the measurement of dc conductivity, and rf conductivity and dielectric constant at 69.25 kMc versus dc bias field, for various n- and p-type germanium samples.

Thus far, complete data runs have been made at room temperature and liquid-nitrogen temperature on eight samples, including the two medium-resistance n-Ge samples discussed in the first quarterly report and a low-resistance n-Ge sample mentioned in the second report. This work included the grinding of 33 filaments on 25 different Ge samples. Fourteen of these filaments were broken in the course of processing and handling, usually after a day or more was spent in preparing the contacts. Of the eight samples tested, only the last two displayed the large ratios of low-temperature to room-temperature conductivity that were expected for these samples. It is believed that the contacts were bad on the first six samples. The last two samples had gold- and nickel-alloyed contacts, replacing the gold-plated contacts used previously. Even though the dc contact was poor for the first two samples, it appears that good rf contact was established capacitively through the interface.

The data for the last two samples are presented in Figs. 7 through 12. One of the samples, No. 304, was an n-Ge sample of about 12 ohm-cm dc room-temperature zero-field resistivity. The other, No. 37, was an 8 ohm-cm p-Ge sample. Figure 7 shows the dc current density versus dc bias field for the p-type sample at 300 and 78°K. These curves are quite similar to plots obtained in the past on similar samples. The corresponding curves for the n-Ge sample, shown in Fig. 8 appear to follow the normal pattern at low fields, but the conductivity rises for fields above a few kv/cm, suggesting that injection of minority carriers may have occurred. Evidence of such injection was found in the shape of the dc current pulses for this sample. At low fields the current pulses were of the same shape as the voltage pulses (bell-shaped), but at high fields the current pulses were roughly the shape of an isosceles triangle. The fact that the current was not constant over

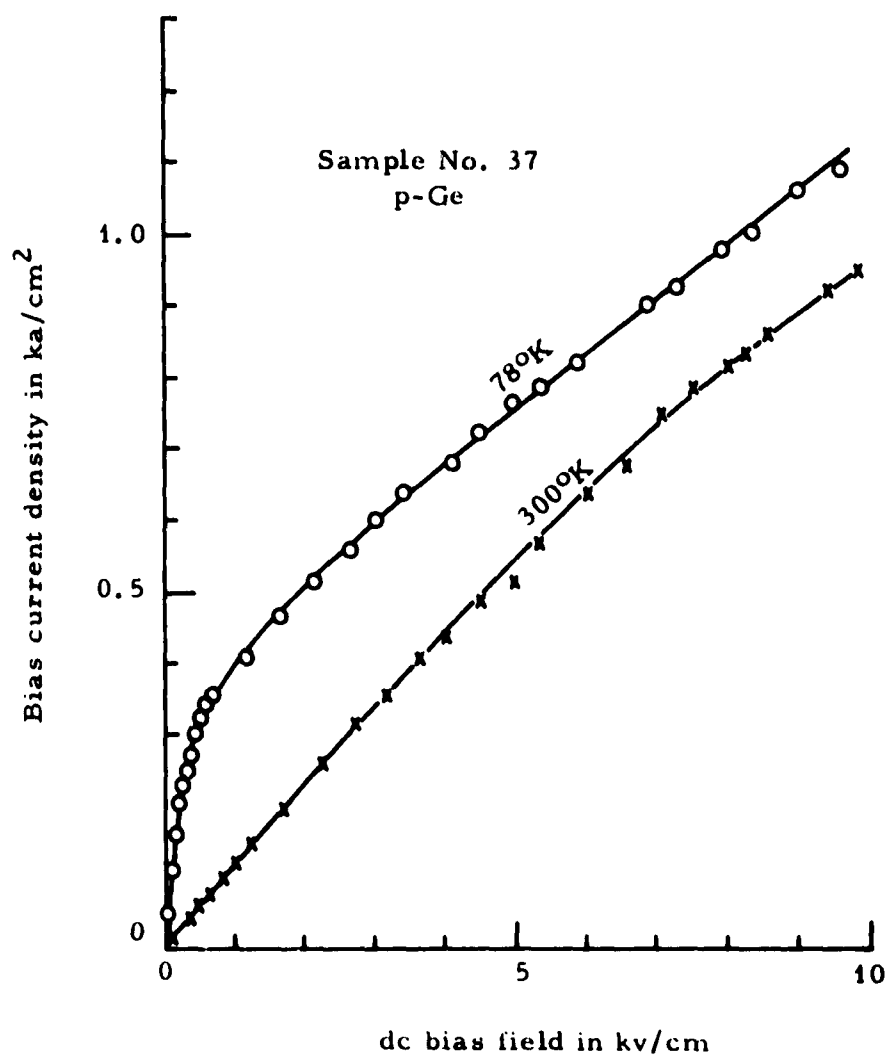


Fig. 7

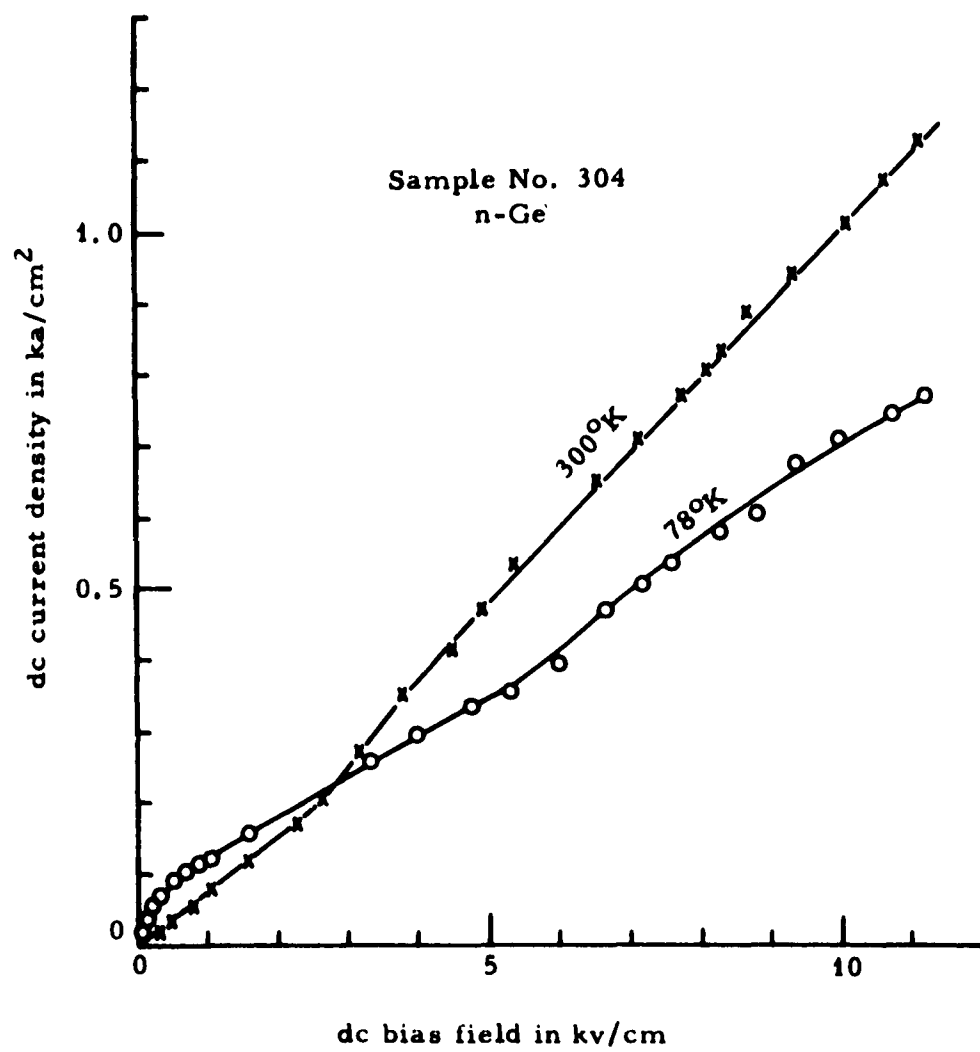


Fig. 8

the flat central portion of the voltage pulse, but instead formed a peak, can be explained by injection; but it must be assumed that such injection occurred throughout most of the bias pulse, which was of only 0.5 microsecond duration. Injection through the top contacts could not be responsible for this, because carriers from this source could not arrive at the filament in less than a few microseconds after application of the bias pulses. It appears that injection may have occurred from the conical portion of the sample just above the thin filament. This could have been caused by the very strong fields obtained in this region as a consequence of the close spacing of the sample and the conical surface in the sample well of the upper waveguide wall. A spacing of 0.005 inch is established between these conical surfaces by means of a thin conical teflon insulator. Therefore, the field at the conical surface of the sample is about 200 kv/cm at the highest voltages used, or about 20 times larger than the field on the filament. Injection is very likely at these field intensities, even though dc contacts are not involved. A method for eliminating possible injection from this source is now being tried. Samples have been prepared with gold plating on the conical portion for purposes of shielding the germanium surface from the large surface fields. This plating will also reduce the rf spreading resistance at the ends of the sample.

Measured values of the small-signal conductivity at 69.5 kMc for the p-Ge and n-Ge samples versus dc field are plotted in Figs. 9 and 10. At room temperature and zero field this conductivity should equal the dc conductivity. Good agreement was obtained for the n-Ge sample, but the value of zero-field room-temperature conductivity obtained for the p-Ge sample was about 70% larger than the dc value. This large discrepancy may be the result of inaccurate correction of the data for rf

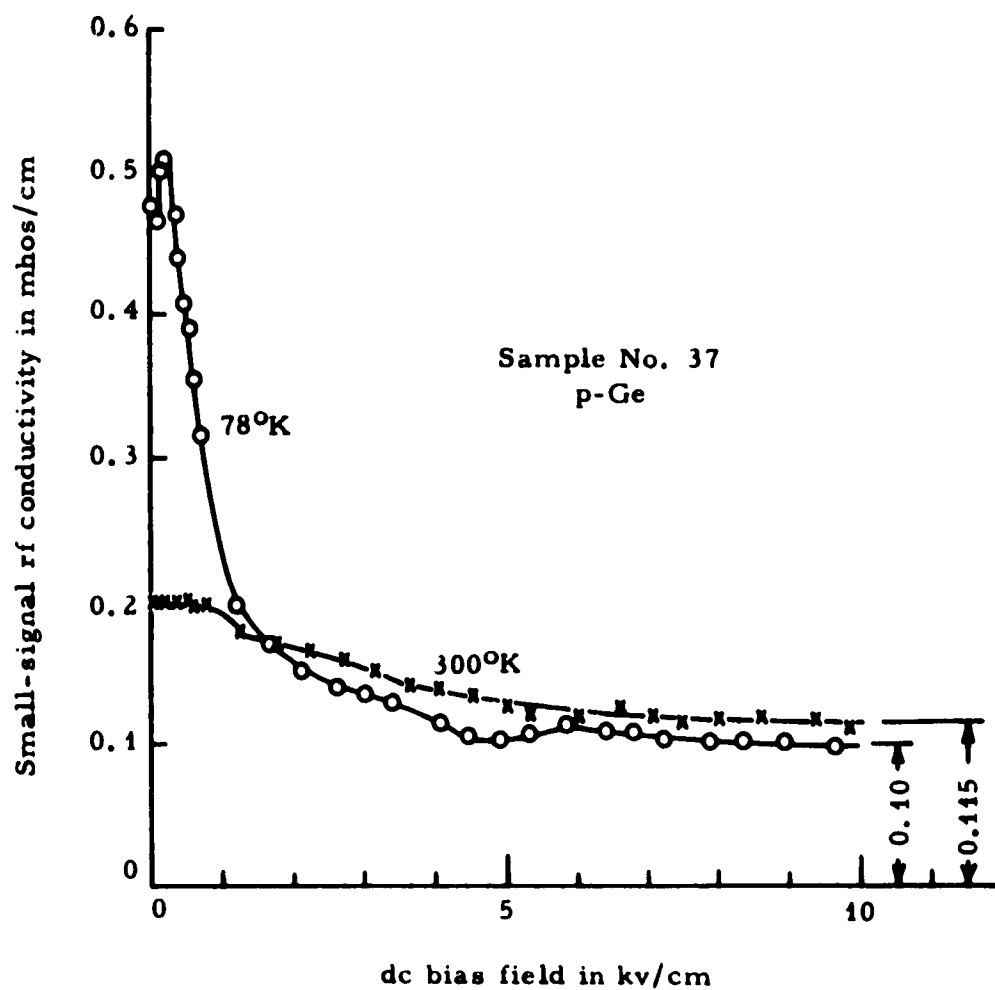


Fig. 9

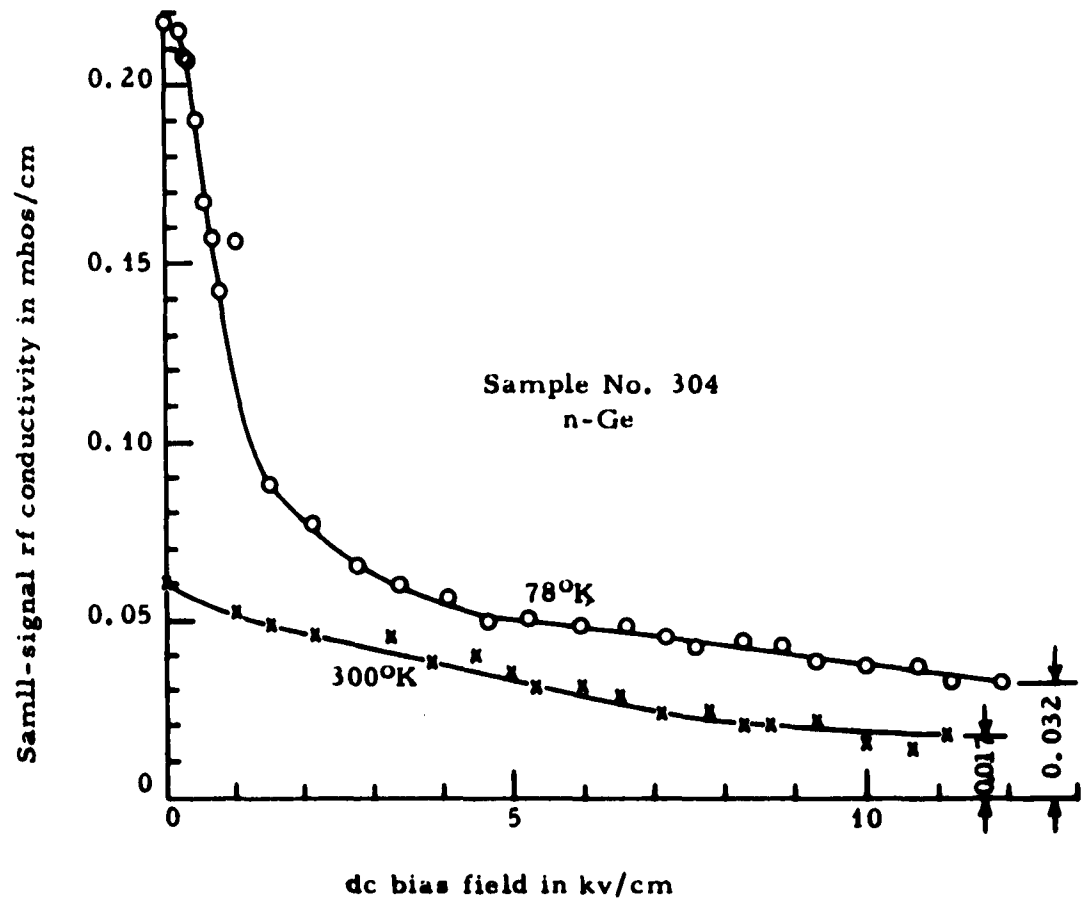


Fig. 10

spreading resistance in the conical ends of the sample. This correction is relatively large and not accurately known for these high-resistance samples. In future tests with gold-plated cones, the rf spreading resistance will be much smaller and will be determined fairly accurately by dc measurements between the gold plating and the filament. Similar measurements will also be made to determine the spreading resistance for samples 37 and 304. Complete evaluation of the data on these samples will be deferred until the data can be reprocessed with more reliable corrections for spreading resistance.

The small-signal rf dielectric constants for the two samples are plotted as functions of the dc bias field in Figs. 11 and 12. The dielectric constants of both samples at 300°K were found to be nearly constant at about the lattice value, as predicted for these low-conductivity samples. The curve obtained for the p-Ge sample at 78°K is very nearly the same as that for a 5 ohm-cm n-Ge sample that we measured some time ago. The dielectric constant of the p-Ge sample started at about 0.7 at zero field and rose very rapidly to nearly the lattice value with fields of less than 2 kv/cm. No overshoot was observed with this sample. The dielectric constant of the n-Ge sample at 78°K started at about 14.5, rose above the lattice value at about 1 kv/cm, decreased slightly, then rose again at fields above about 3 kv/cm to a maximum of 22. It is possible that injection may have been responsible for this anomalous behavior, either through the effects of the minority carriers in the filament or through variation in the spreading resistance, which is large enough to affect the dielectric constant as well as the conductivity data. The observed overshoot in the n-Ge sample and the lack of overshoot in the p-Ge sample are in agreement with results obtained at about 35 kMc by Gibson, Granville, and Paige.¹⁰ It is planned to repeat the measurements on n-Ge sample 304 with its cone gold plated to avoid injection and spreading resistance errors so that the true behavior of the dielectric constant at high fields can be observed.

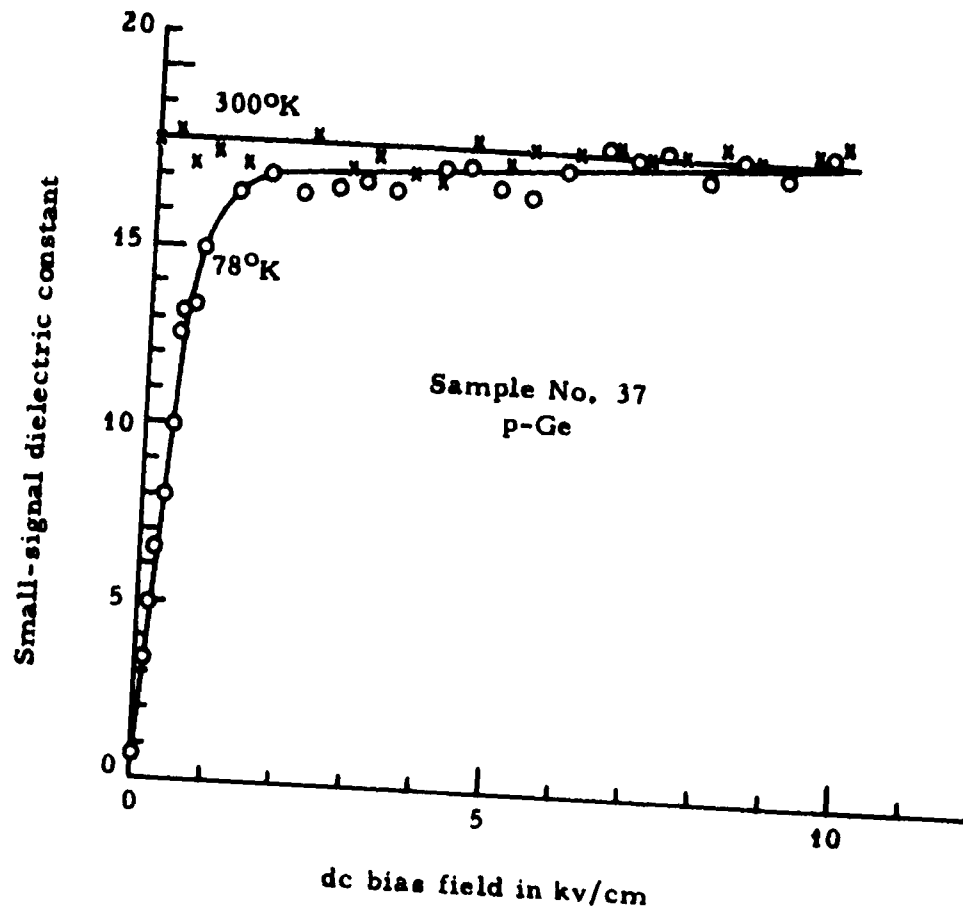


Fig. 11

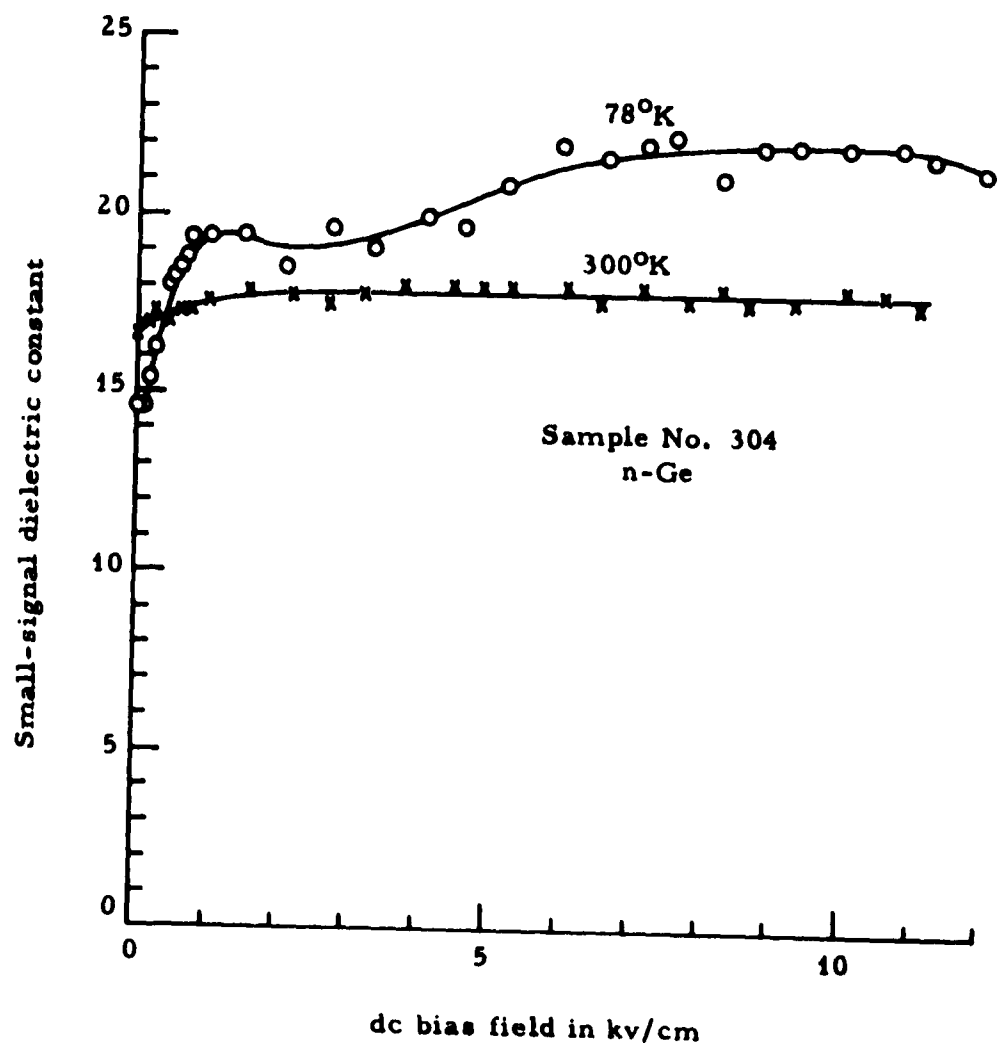


Fig. 12

1.3.2 Preparation of InSb Samples

A 50-gram boule of InSb was purchased during the last quarter. In seeking further information on this material from the vendor we learned that grinding and sawing drives dislocations into the material to a depth of about 1/4 inch, resulting in greatly decreased mobility. This damage can be avoided by cutting the boule with a diamond-charged string, but unfortunately this method cannot be adapted to the fabrication of the special sample shapes required for our microwave measurements. Therefore, alternative methods for sample preparation had to be considered.

It was decided to try electrical-discharge machining of the material, using the facilities of a job shop equipped with an Elox EDM machine. Preliminary cuts were made with scrap pieces of InSb, and it was found that it can be cut very well by the EDM process. Several cylinders slightly larger than the required final body diameter were then cut from the new boule. Conductivity and Hall-effect measurements were performed on one of these while attempts were made to complete the machining on the others to form the cones and filaments. The 78°K mobility, determined from the conductivity and Hall-effect measurements, was about an order of magnitude smaller than the value specified by the InSb supplier. Tests are now being made on the original boule to determine whether this low mobility is characteristic of the original material or a result of the processing. Meanwhile, attempts at forming thin filaments by EDM met with considerable difficulty, and it was decided to accept samples with 0.050-inch filaments and use etching techniques to reduce the filament diameter to 0.010 inch. Two samples were made this way. Etching resulted in filaments of triangular cross section, since the material has a 111 orientation, but these are uniform enough for good quantitative measurements. Rf tests will be performed on these samples, even though the mobility is apparently low.

PROGRAM FOR NEXT QUARTER

The effect of field on recombination will be measured in additional copper- and nickel-doped p-germanium samples, as well as in copper-doped n-germanium. Surface effects will be investigated further to enable us to correct for them. Measurements will be made on samples with lifetime determined by recombination at dislocations. When the data are well established, further thought will be given to the interpretation of the capture cross section results.

Additional measurements at 69 kMc will be made on germanium samples. Gold plating will be used on the cones to avoid injection and to reduce the rf spreading resistance. This resistance will be determined by dc measurements between the plated cone and the base of the filament. With the exception of the repetition of measurements on the high-resistivity n-Ge sample, future work will be confined to heavily doped n-Ge samples, for which the most useful types of nonlinearity are expected, using various orientations.

Attempts will be made to obtain quantitative comparisons between the complex conductivity data and predictions based upon the energy relaxation equations and to find empirical values for τ_c and τ_m for comparison with values expected from theoretical considerations.

Further measurements will be made on InSb to assess the effects of EDM machining. These will include rf complex conductivity measurements on the two filamentary samples that were prepared by EDM and etching. If the results of these measurements show that the properties of InSb are seriously affected by EDM, then alternative methods of sample fabrication will be investigated.

FISCAL INFORMATION

<u>Contract Value</u>	<u>Amount Spent through</u> <u>2/28/62</u>	<u>Balance</u>
\$ 47,520.	\$ 39,527.	\$ 7,993.

Man hours expended by individuals

<u>Name</u>	<u>Hours</u>
E. Conwell	130
L. Vivenzio	92
J. Zucker	399
V. Fowler	194
A. Willis	<u>380</u>
Total Hours	1,195

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<p>General Telephone & Electronics Laboratories Inc., Bayshore, N.Y., HOT CARRIER PHENOMENA IN SEMICONDUCTORS AT MICROWAVE FREQUENCIES, by E. M. Conwell, V. J. Fowler and J. Zucker. Third Quarterly Report, Nov. 15, 1961 - Feb. 15, 1962, 42 pp. incl. illus. Signal Corps Contract No. DA 36-039-SC 87298. Unclassified Report.</p> <p>An expression is derived for the diffusion constant $D(i)$ of thermal carriers in the ith valley of a many-valley semiconductor. The Einstein relation is shown to hold between $D(i)$ and $\mu(i)$, the mobility tensor for the ith valley. In n-Ge intervalley scattering is sufficiently rapid so that the actual diffusion rate depends on the average of $D(i)$ over the valleys, which is a scalar. The same result is obtained for $D(i)$ when a high electric field is applied perpendicular to the concentration gradient, except that the average must be taken over the actual energy distribution of carriers in the high field. At 3 kMc the time variation of the field is slow enough so that the instantaneous D should be equal to D for a dc field of the same magnitude. For measurements of recombination in high electric fields the method of injection has been changed from surface illumination to point-contact injection. Data on recombination, conductivity and dielectric constant were obtained for high-frequency fields. Some anomalies are mentioned.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Diffusion of Excess Carriers in a Many-Valley Band Structure 2. Investigation of Recombination of Hot Carriers 3. Complex Conductivity Investigation 	<p>General Telephone & Electronics Laboratories Inc., Bayshore, N.Y., HOT CARRIER PHENOMENA IN SEMICONDUCTORS AT MICROWAVE FREQUENCIES, by E. M. Conwell, V. J. Fowler and J. Zucker. Third Quarterly Report, Nov. 15, 1961 - Feb. 15, 1962, 42 pp. incl. illus. Signal Corps Contract No. DA 36-039-SC 87298. Unclassified Report.</p> <p>An expression is derived for the diffusion constant $D(i)$ of thermal carriers in the ith valley of a many-valley semiconductor. The Einstein relation is shown to hold between $D(i)$ and $\mu(i)$, the mobility tensor for the ith valley. In n-Ge intervalley scattering is sufficiently rapid so that the actual diffusion rate depends on the average of $D(i)$ over the valleys, which is a scalar. The same result is obtained for $D(i)$ when a high electric field is applied perpendicular to the concentration gradient, except that the average must be taken over the actual energy distribution of carriers in the high field. At 3 kMc the time variation of the field is slow enough so that the instantaneous D should be equal to D for a dc field of the same magnitude. For measurements of recombination in high electric fields the method of injection has been changed from surface illumination to point-contact injection. Data on recombination, conductivity and dielectric constant were obtained for high-frequency fields. Some anomalies are mentioned.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Diffusion of Excess Carriers in a Many-Valley Band Structure 2. Investigation of Recombination of Hot Carriers 3. Complex Conductivity Investigation 	<p>UNTERMS</p> <p>Semiconductor Germanium Doping Carriers, hot Carriers, diffusion Carriers, recombination Conductivity, high frequency Photocurrent Capture cross section Dielectric constant</p>
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Carriers, recombin-
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Capture cross section
Dielectric constant**

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